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(54) BATTERY AND MANUFACTURE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a high-performance battery of excellent charge/discharge characteristics, performance stability, and safety as a battery using high polymer solid electrolyte having a bridge structure, and manufacturing method for that.

SOLUTION: In a battery in which a positive electrode and a negative electrode connected through polymer solid electrolyte including polyvinylidene fluoride having a bridge structure and/or vinylidene fluoride copolymer, at least the positive electrode has a collector, where the collector of at least one electrode is a porous collector, or otherwise, the positive electrode and the negative electrode are laminated through a separator to form a laminated body, in which electrolyte is impregnated.

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CLAIMS

[Claim(s)]
[Claim 1] It is the cell which a positive electrode and a negative electrode are joined through the solid polymer electrolyte containing the polyvinylidene fluoride which has the structure of cross linkage, and/or a vinylidene fluoride system copolymer, and a positive electrode at least has a charge collector, and is characterized by one [at least] charge collector being a perforated charge collector.
[Claim 2] A positive electrode at least is the manufacture approach of the cell according to claim 1 characterized by carrying out a laminating on both sides of the separator containing the polyvinylidene fluoride which has a charge collector and has the structure of cross linkage for the positive electrode and negative electrode one [at least] charge collector of whose is a perforated charge collector, or a vinylidene fluoride system copolymer, and infiltrating the electrolytic solution into this layered product after forming a layered product.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the cell which used the solid polymer electrolyte.
[0002]
[Description of the Prior Art] Since the cell which uses a solid polymer electrolyte as an ionic migration medium does not have a liquid spill compared with the cell which uses the conventional electrolytic solution as an ionic migration medium, while the dependability of a cell and safety improve, that the ease of thin-film-izing or layered product formation and the degree of freedom of a cell gestalt are high, simplification of a package, and lightweight-ization are expected.
[0003] The ingredient which added the electrolyte and the plasticizer as this giant-molecule solid electrolyte ingredient to ion conductivity polymers, such as an ingredient centering on polyalkylene oxide, such as polyethylene oxide and polypropylene oxide, a polyacrylonitrile, and a polyvinylidene fluoride system ingredient, is proposed. When using for a cell using this solid polymer electrolyte ingredient, it is desirable that a solid polymer electrolyte is excellent in high ion conductivity, high intensity, thermal resistance, electrochemical stability, etc. The mixture which added the plasticizer is used for the mixture with which the solid polymer electrolyte consisted of a matrix polymer and an electrolyte, or this ingredient. Various polymers are proposed as this matrix polymer (for example, Gray work, a polymer ingredient given in SolidPolymer Electrolytes (VCH pub RISSHA: 1991)). Among these, since the solid polymer electrolyte ingredient using vinylidene fluoride system polymers, such as polyvinylidene fluoride and a vinylidene fluoride system copolymer, especially as a matrix polymer is excellent also in which the above-mentioned point, it is desirable.
[0004] The cell using a solid polymer electrolyte can process a predetermined configuration, and can produce the layered product to which the laminating of sheet-like an electrode and a solid polymer electrolyte was carried out, and the layered product to which the electrode surface was made to carry out the after [spreading formation] laminating of the solid polymer electrolyte layer. Moreover, the approach of forming each class of an electrode / solid polymer electrolyte / electrode by coating is also proposed. Thus, since approaches, such as a sheet lamination and coating, are employable, it is expected that a manufacture process is excellent in mass-production nature. Moreover, since the liquid spill which may happen by the conventional electrolytic-solution system cell does not happen substantially, production process management is easy, and high-voltage-ization by the series connection laminating of an electrode / solid polymer electrolyte / electrode layered product is also expected.
[0005] The cell which used the Pori (hexafluoropropylene-vinylidene fluoride) copolymer for the giant-molecule solid electrolyte is proposed (U.S. Pat. No. 5296318 specification). Although said vinylidene fluoride system copolymer was used as this giant-molecule solid electrolyte, since it did not have the structure of cross linkage, it was lacking in thermal stability, and since it had melting nature and solubility, it was a problem with practical cell safety. Moreover, when sinking in and using for the non-aqueous-solvent system electrolytic solution as the production approach of this cell, using said copolymer sheet as a separator, since melting and the dissolution took place in elevated-temperature sinking in, sinking-in temperature was restricted, the amount of electrolytic-solution swelling to the inside of a polymer stopped low by this, and ionic conductivity was low. In order to improve this, a cross-linking monomer is made to contain in vinylidene fluoride system polymer structure, and the structure-of-cross-linkage formation by the monomer polymerization is proposed (U.S. Pat. No. 5429891 specification). However, depending on the monomer, the electrochemistry side reaction by the

polymer of a residual monomer or a cross-linking monomer and the hydrolysis by the water of a minute amount occurred, and electrochemical side reaction might be caused in connection with it. Moreover, in order to distribute such a cross-linking monomer in a polymer matrix, the organic solvent solution needed to be used, there was a problem that working temperature was restrained in consideration of the polymerization of a monomer, and since this polymerization process was complicated, it was an industry top problem.
[0006] Using for a rechargeable battery the electrode formed on the other hand on the charge collector which has perforation is proposed, and the adhesion of a charge collector and an electrode active material and current collection nature are improved (JP,7-70327,B). Moreover, using this perforated charge collector in the solid polymer electrolyte cell which made the vinylidene fluoride system copolymer the polymer matrix is proposed (U.S. Pat. No. 5470357 specification). However, problems, like the electrochemistry side reaction by the same aforementioned residual monomer as the solid polymer electrolyte using a vinylidene fluoride system copolymer and an aforementioned cross-linking monomer polymer occurs were left behind.
[0007]
[Problem(s) to be Solved by the Invention] It aims at offering the cell which was excellent in a charge-and-discharge property, engine-performance stability, and safety using the solid polymer electrolyte.
[0008]
[Means for Solving the Problem] this invention persons advanced research of the solid state battery which used the solid polymer electrolyte, and completed the cell of this invention. That is, this invention is as follows.
(1) It is the cell which a positive electrode and a negative electrode are joined through the solid polymer electrolyte containing the polyvinylidene fluoride which has the structure of cross linkage, and/or a vinylidene fluoride system copolymer, and a positive electrode at least has a charge collector, and is characterized by the charge collector of one [at least] electrode being a perforated charge collector.
(2) A positive electrode at least is the manufacture approach of the cell the above 1 characterized by carrying out a laminating on both sides of the separator containing the polyvinylidene fluoride which has a charge collector and has the structure of cross linkage for the positive electrode and negative electrode one [at least] charge collector of whose is a perforated charge collector, or a vinylidene fluoride system copolymer, and infiltrating the electrolytic solution into this layered product after forming a layered product.
[0009] Hereafter, this invention is explained to a detail. It is characterized by being the perforated charge collector with which the cell of this invention consists of the positive electrodes, solid polymer electrolytes, and negative electrodes which were formed on the charge collector, it does not need to be even if this negative electrode has the charge collector, and one [at least] charge collector of this positive electrode and a negative electrode has a through tube. By the through tube of this perforated charge collector, it not only makes it easy to electrolytic-solution sink in to the polar zone and/or the separator section of a layered product which consist of a positive electrode / a separator, or a solid polymer electrolyte/negative electrode, but it can aim at resistance reduction of an electrode. The separator stated by this invention is the solid polymer electrolyte precursor which can be used as a solid polymer electrolyte by sinking in and swelling the electrolytic solution, i.e., the Plastic solid which consists of resin for solid polymer electrolytes before sinking in and swelling with the electrolytic solution.
[0010] As for a positive electrode at least, in the cell of this invention, it is desirable to have the structure where the charge collector with which electrode active material powder becomes the layer formed by the mixture distributed with the binder from a right electric conduction object was joined. The layer in which this electrode active material powder was formed by the mixture distributed with the binder may exist only in one side of a charge collector, and may exist in both sides.
[0011] After joining an electrode active material layer to the approach of joining an electrode active material layer to the charge collector of the structure containing holes, such as a mesh, textile fabrics, a nonwoven fabric, and a sintered compact, as the typical production approach of an electrode of having this perforated charge collector, the approach of making form a hole in the charge collector which consists of a continuum beforehand, and joining an electrode active material layer to it, and the charge collector that consists of a continuum, the method of performing drilling processing of a charge collector etc. is mentioned. As this charge collector ingredient, the ingredient which was excellent in the positive electrode at oxidation stability is desirable, aluminum, stainless steel, nickel, carbon, etc. are used and especially aluminum is desirable. Moreover, as a charge collector ingredient of a negative electrode, metal copper, stainless steel, nickel, carbon, etc. are used,

and especially metal copper is desirable.
[0012] As a perforated charge collector used by this invention, it has 1.5mm or less of average apertures, and the penetrated hole 100A or more, and it is desirable that they are 5% or more of numerical apertures and 90% or less. If an average aperture is larger than 1.5mm, a current collection operation of a charge collector is not enough, and desirable from reducing the mechanical strength of an electrode. Moreover, since it becomes difficult in less than 100A to electrolytic-solution sink in an average aperture, it is not desirable. In the case of less than 5% of numerical apertures, if electrolytic-solution sinking in becomes difficult and the effectiveness [active material layer / a charge collector and / electrode] of the improvement in adhesion and a resistance reduction operation of an electrode fully exceed 90% of numerical apertures, it is not desirable from a current collection operation of a charge collector becoming less enough. As for the thickness of a charge collector, it is still more desirable that it is 500 micrometers or less. Since the volume energy density of the cell constituted by the appearance volume of the charge collector itself becoming large using this will fall if thicker than 500 micrometers, to a small lightweight rechargeable battery, it is not desirable.
[0013] Moreover, the polymer matrix of the giant-molecule solid electrolyte in this invention needs to contain the polyvinylidene fluoride which has the structure of cross linkage, and/or a vinylidene fluoride system copolymer. As a vinylidene fluoride system copolymer, for example The Pori (hexafluoropropylene-vinylidene fluoride) copolymer, The Pori (perfluoro vinyl ether-vinylidene fluoride) copolymer, The Pori (tetrafluoroethylene-vinylidene fluoride) copolymer, The Pori (hexafluoro propylene oxide-vinylidene fluoride) copolymer, The Pori (hexafluoro propylene oxide-tetrafluoroethylene-vinylidene fluoride) copolymer, The Pori (hexafluoropropylene-tetrafluoroethylene-vinylidene fluoride) copolymer and the Pori (fluoro ethylene-vinylidene fluoride) copolymer are mentioned. An independent object or a mixture can also use these polyvinylidene fluorides and a vinylidene fluoride system copolymer. As for the content of the vinylidene fluoride unit in the polymer matrix of the giant-molecule solid electrolyte used by this invention, it is desirable that it is 20 % of the weight or more, and it is more desirable that it is 50 % of the weight or more. Moreover, the layered product which carried out the laminating of polyvinylidene fluoride and/or a vinylidene fluoride system copolymer, and other polymers as a giant-molecule solid electrolyte polymer matrix in the cell of this invention is also usable.
[0014] When a solid polymer electrolyte has the structure of cross linkage in this invention, while excelling in thermal resistance and dimensional stability, the ingredient of a high electrolytic-solution content is obtained, and this brings about high ionic conductivity and serves as a desirable ingredient. When formed by the polymer over which the polymer matrix of a solid polymer electrolyte is not constructing a bridge, in the case of the boosting charge of a cell, or rapid discharge, or heat tracing, were easy to flow, the inter-electrode short circuit was sometimes caused [melting and] in connection with this, and there was an insurance top problem of a cell. In the solid polymer electrolyte containing the vinylidene fluoride system polymer which, on the other hand, has the structure of cross linkage of this invention, such a problem is avoidable.
[0015] Polyvinylidene fluoride system resin usually has linear structure, and produces the matrix polymer of the polyvinylidene fluoride system resin of this invention by bridge-formation-izing this resin. The approach of making contain the radiant-energy exposure of an electron ray, a gamma ray, an X-ray, ultraviolet rays, infrared radiation, etc. and a radical initiator, and carrying out reaction bridge formation, the method of carrying out reaction bridge formation of the alkali treatment (deHF) back reactivity radical, etc. can be used as this bridge formation approach. As a cross-linking condition in the case of using electron beam irradiation, when this exposure is not enough, the bridge formation effectiveness is not enough, and since polymer structure collapses when there are too many exposures, it is not desirable. It is desirable still more desirable that it is [5 or more Mrads] 100 or less Mrad, and this exposure is 5 or more-Mrad 80 or less Mrad.
[0016] This structure-of-cross-linkage formation can be checked by the solubility to a linear-polymer fusibility organic solvent. That is, the polyvinylidene fluoride system resin with which the structure of cross linkage was formed has the component which does not dissolve in a fusibility organic solvent, and since it does not carry out the homogeneity dissolution, it can distinguish the existence of the structure of cross linkage. It has the component which does not dissolve having the structure of cross linkage in this invention in a fusibility organic solvent, and what does not carry out the homogeneity dissolution is said. Although it is not limited since this fusibility solvent changes with polymer classes, it can distinguish, for example with solvents, such as N-methyl pyrrolidone, chloroform, dichloromethane, a dichloroethane, an acetone, a tetrahydrofuran, dimethylformamide,

dimethyl sulfoxide, and dimethylacetamide.
[0017] The solid polymer electrolyte which sank in and formed the electrolytic solution in a bulk configuration, the porous body which has a through tube, the foam which has an independent bubble as a giant-molecule solid electrolyte can be used. Among these, the solid polymer electrolyte which infiltrated the electrolytic solution into the porosity polymer which has the solid polymer electrolyte which sank the electrolytic solution into the foam containing an independent bubble, and a through tube forms into structure a composite construction with the polymer phase which has a liquid phase domain, and was sunk in and swollen with the electrolytic solution. It is desirable from the ionic conductivity of a solid polymer electrolyte being raised by existence of this liquid phase, and bringing about ionic conductivity high as a whole.
[0018] As an electrolyte contained in the electrolytic solution used by this invention, both an organic acid organic salt an inorganic acid and mineral salt are usable. The metal salt of organic acids, such as inorganic acids, such as tetrafluoroboric acid, perchloric acid, a sulfuric acid, a phosphoric acid, a hydrofluoric acid, and a hydrochloric acid, trifluoro methansulfonic acid, a truffe TSUORO propyl sulfonic acid, screw (trifluoromethane sulfonyl) imido acid, an acetic acid, chill gifblaar poison, and a propionic acid, and these organic acids, and an inorganic acid is mentioned as this example. These can also be used independently, and can also mix and use two or more electrolytes. Furthermore, a perfluoro sulfonic-acid system polymer, perfluoro carboxylic-acid system polymers, or these metal salts can also be used as an electrolyte of this invention. It is one kind, and the cation chosen from a proton, an alkali-metal cation, an alkaline earth metal cation, a transition-metals cation, a rare earth metal cation, etc. as a cation of these electrolytes can be used, mixing more than one. Since this cation kind changes with applications to be used, it is not limited. For example, when using the giant-molecule solid electrolyte of this invention for a lithium cell, it is desirable to use lithium salt as an electrolyte to add. It is desirable to choose as an electrolyte the lithium salt which is rich in electrochemical stability from the need of carrying out by repeating charge and discharge when using especially for a lithium secondary battery. As this example CF3 SO3 Li, C4 F9 SO3 Li, 2 (CF3 SO2) NLi, LiBF4, LiPF6, LiClO4 and LiAsF6, Li(C six H5)4 B, Li2 B10Cl10, and Li2 B12Cl12 grade can be mentioned.
[0019] Moreover, a plasticizer can be made to contain for the purpose, such as improvement in workability of a solid polymer electrolyte which raises ionic dissociation promotion of the electrolyte which sank into the solid polymer electrolyte of this invention, and electrolytic impregnating ability. In the solid polymer electrolyte with which the bridge was constructed over this invention, it has the description which does not spoil dynamic reinforcement in a high plasticizer content. Although it is not limited since this plasticizer content changes with the class of plasticizer, the class of vinylidene fluoride system polymer, and structures, it is usually 98% or less of solid polymer electrolyte weight. It is 97% or less still more preferably.
[0020] As an example of this plasticizer, ethylene carbonate, propylene carbonate, Annular carbonate, such as BICHIREN carbonate, dimethyl carbonate, Chain-like carbonate, such as methylethyl carbonate and methylethyl carbonate, The ether, such as a tetrahydrofuran and a methyl tetrahydrofuran, gamma-butyl lactone, Nitryl compounds, such as ester, such as propiolactone and methyl acetate, an acetonitrile, and propionitrile, Organic low molecular weight compounds, such as a hydrocarbon, a silicone oil, oligo ethylene glycol, Polar-group content macromolecule organic compounds, such as aliphatic series ETARU compounds, such as polyethylene oxide and polypropylene oxide, a polyacrylonitrile, aliphatic series polyester, and an aliphatic series polycarbonate, can be mentioned.
[0021] The solid polymer electrolyte of this invention is produced by sinking into the Plastic solid which consists of vinylidene fluoride system resin with which a bridge formation object and the body non-constructed a bridge mixed the electrolyte explained above and the electrolytic solution which consists of a plasticizer. Next, the electrode joined through the solid polymer electrolyte of this invention is explained. For example, when a cell is a lithium cell, the matter in which lithium ion occlusion emission is possible is used for the positive electrode and negative electrode of an electrode. As the ingredient which has high potential to a negative electrode as this positive-electrode matter, and this example Li1-x CoO2, Ln1-x NiO2, Li1-x Mn 2O4, Li1-x MO2 (0< x<1), and M express the mixture of Co, nickel, Mn, and Fe. Li2-y Mn 2O4 (0< y<2) and crystalline Li1-x V 2O5, the shape of amorphous -- the oxide (0<x'<1.2) of Li2-y V 2O5 (0< y<2), Li1.2-x'Nb 2O5, etc. -- The metal (0< z<3) chalcogenide of Li1-x TiS2, Li1-x MoS2, Li3-z NbSe3, etc., Organic compounds, such as polypyrrole, the poly thiophene, the poly aniline, the poly acene derivative, polyacethylene, poly thienylene vinylene, the poly propine vinylene, a dithiol derivative, and a disulfide derivative, can be

mentioned.
[0022] Moreover, the ingredient which has low potential to the above-mentioned positive electrode as a negative electrode is used. As this example, metal lithiums, such as a metal lithium, an aluminum lithium alloy, and a magnesium aluminum lithium alloy, Carbon system ingredients, such as an intermetallic compound of AlSb, Mg<SUB>2 germanium, NiSi2, etc., graphite, corks, and a low-temperature baking macromolecule, a SnM system oxide (M expresses Si, germanium, and Pb.) Si1-y M'y Oz (M' expresses W, Sn, Pb, B, etc.) The lithium solid solution of metallic oxides, such as a multiple oxide, titanium oxide, and ferrous oxide, Ceramics, such as a nitride of Li7 MnN4, Li3 FeN2, Li3-x Cox N, Li3-x NiN, Li3-x Cux N, Li3 BN2, Li3 AlN2, and Li3 SiN3, etc. is mentioned. However, since what is necessary is just the ingredient which has conductivity when returning a lithium ion with a negative electrode and using as a metal lithium, it is not limited above.
[0023] The positive electrode and negative electrode which are used for the cell of this invention carry out fabrication of the above-mentioned ingredient to a predetermined configuration, and are used. Either a continuum or the binder dispersing element of a powder ingredient is usable as this gestalt. As the shaping approach of the former continuum, electrolytic deposition, the electrolysis dissolution, vacuum evaporationo, sputtering, CVD, melting processing, sintering, compression, etc. are used. Moreover, in the case of the latter, powder-like electrode material is mixed and fabricated with a binder. As this binder ingredient, hydrocarbon system polymers, such as fluorine system polymers, such as polyvinylidene fluoride system resin, such as polyvinylidene fluoride and the Pori (hexafluoropropylene-vinylidene fluoride) copolymer, and polytetrafluoroethylene, a styrene-butadiene copolymer, a styrene acrylonitrile copolymer, and a styrene-acrylonitrile-butadiene copolymer, a polymer precursor, a metal, etc. are used, and the polyvinylidene fluoride system resin which has the structure of cross linkage of this invention can also be used for a binder.
[0024] as the production approach of the cell of this invention -- ** -- after carry out the laminating of the solid polymer electrolyte, the positive electrode, and the negative electrode which sank in and produced the electrolytic solution to the polymer matrix beforehand, carry out the laminating of the approach of forming a layered product and constituting an unit cell, the separator which is the precursor of ** solid polymer electrolyte, a positive electrode, and the negative electrode and forming a layered product, the approach of making a separator sink in and swell the electrolytic solution, making change a separator into a solid polymer electrolyte and forming an unit cell, those with **, and all are possible Especially in the case of the latter, if it takes into consideration that the electrolytic solution tends to deteriorate at the humidity which exists in an ambient atmosphere, simple [of the ambient atmosphere management process] can be carried out, and it is desirable on industry. Moreover, since the effectiveness that an electrode hole part is filled up with the electrolytic solution by electrolytic-solution sinking in, and electrode resistance reduction and electrochemical junction of an electrode and a solid polymer electrolyte become good by this is also considered, also in the former unit cell production approach, it is effective after layered product formation to give to electrolytic-solution sink in. Since electrolytic-solution sinking in in the making process of the unit cell of such this invention is preferably performed when it is the structure where the electrode which has a perforated charge collector consists of electrode active material powder and a binder, as for the electrode which has a perforated charge collector, it is desirable that it is the structure which consists of electrode active material powder and a binder. When the electrode which has a perforated charge collector is a continuum, sinking in to a separator becomes difficult. However, when not infiltrating the electrolytic solution behind an electrode laminating in an unit cell making process, since the electric resistance of a charge collector and an electrode layer to connect has the effectiveness which can be reduced, it can constitute the cell of this invention from various approaches using various ingredients as an electrode material.
[0025] Although it is suitable for a lithium ion battery, since especially the cell of this invention does not remain in this but can be applied to various cells, such as a lead cell, an alkaline cell, and a nickel hydoride battery, it is useful on industry.
[0026]
[Embodiment of the Invention] Hereafter, an example explains this invention to a detail.
[0027]
[Example 1] the needle coke powder of 10 micrometers of mean diameters -- a carboxymethyl-cellulose solution and styrene butadiene latex (Asahi Chemical Industry Co., Ltd. make, L1571 trade name) dispersion liquid -- it distributed to the mixture and the slurry was produced, spreading desiccation was carried out and the

paint film (one side coating) of 120 micrometers of thickness was formed in the metal copper sheet (18-micrometer thickness). The presentation in this paint film was set to (needle coke NC) / carboxymethyl-cellulose / styrene butadiene =100/0.8/2. from the current collection dignity of this electrode sheet -- ****(ing) -- a hole with an average diameter of 150 micrometers -- 1cm2 The electrode which consists of a perforated charge collector opened per 625 pieces was produced. On the other hand, it is $LiCoO_2$ of 10 micrometers of mean diameters. Mixed distribution of powder and the carbon black was carried out at N-methyl pyrrolidone solution (5 % of the weight) of polyvinylidene fluoride, and the slurry was produced. Spreading (one side coating) desiccation of this slurry was carried out at aluminum foil (20-micrometer thickness), and the paint film of 100 micrometers of thickness was produced. In addition, solid content weight composition of a slurry was made into $LiCoO_2$ (85%), carbon black (8%), and a polymer (7%). Subsequently, the aluminum charge collector side of an electrode sheet to 1cm2 The electrode which forms the hole of 625 hits (average diameter of 150 micrometers) by needling, and consists of a perforated charge collector was created. Subsequently, this NC electrode and $LiCoO_2$ The electrode was disconnected on 5cm square, respectively.

[0028] It is melting push, the Pori (hexafluoropropylene-vinylidene fluoride) copolymer (5 % of the weight of hexafluoropropylene contents) was fabricated, and the sheet of 110 micrometers of thickness was produced. After giving electron beam irradiation (exposure 10Mrad) to this polymer sheet, chlorofluocarbon (HFC134a) was infiltrated (7% of sinking-in weight), it heated in the state of sinking in, and foam was produced (220 micrometers of after [foaming] thickness). This sheet was immersed in the $LiBF_4$ 1.5 mol/l. solution of (ethylene carbonate EC) / (propylene carbonate PC) / gamma-butyl lactone (gamma-BL) mixed solvent (EC/PC/gamma-BL =1/1/2) for 1 hour, the electrolytic solution was infiltrated, and the solid polymer electrolyte sheet was produced.

[0029] NC electrode and $LiCoO_2$ which were cut on the aforementioned 5cm square after cutting this solid polymer electrolyte sheet on 5.5cm square It was made to rival with the structure of opposing the paint film side of an electrode to a solid polymer electrolyte, and the cell layered product was produced. Subsequently, the $LiBF_4$ 1.5 mol/l. solution of (ethylene carbonate EC) / (propylene carbonate PC) / gamma-butyl lactone (gamma-BL) mixed solvent (EC/PC/gamma-BL =1/1/2) was made immersed in this layered product for 10 seconds. The stainless steel sheet was joined to the metal copper sheet surface and the aluminium sheet side as an electrode for electrode ejection from the layered product after electrolytic-solution sinking in, it packed with polyethylene / aluminum / polyethylene terephthalate laminating sheet further, and the sheet cell was produced. This cell was connected to the terminal of a charge and discharge test machine (Hokuto Denko 101SM6 mold), and charge and discharge were performed. As charge-and-discharge conditions, 25mA of currents performed charge by back 4.2V constant potential charge of 25mA of currents, and constant current, and discharge was performed by 2.7 V cuts. Charge-and-discharge effectiveness (quantity of electricity) was the time [2nd] 80% of first time and 98%, and the first-time amount of discharge was 216 mAh/g per carbon weight of a negative-electrode electrode. As a result of repeating a charge-and-discharge cycle furthermore, the percentage to the amount of first time charge-and-discharge discharge of the amount of discharge in 100 cycle (quantity of electricity) was 84%.

[0030]

[Example 2] To the metal copper used in the example 1, and each aluminum charge collector sheet, it is a hole with a diameter of 150 micrometers 1cm beforehand 2 The perforated charge collector sheet formed per 625 pieces is produced, spreading formation is carried out like [this one side] an example 1, and it is a needle coke electrode (negative electrode) and $LiCoO_2$. The electrode (positive electrode) was produced. The electrode sheet of the positive electrode in which the electrode paint film was formed on the perforated charge collector, and a negative electrode was cut on 5cm square, respectively. It is melting push, the Pori (hexafluoropropylene-vinylidene fluoride) copolymer (1.4 % of the weight of hexafluoropropylene contents) was fabricated, and the sheet of 45 micrometers of thickness was produced. Electron beam irradiation (exposure 30Mrad) was given to this polymer sheet. After cutting the sheet after electron beam irradiation on 5.5cm square, the layered product consisted of structures of making the paint film side of the electrode sheet of the positive electrode produced in the top, and a negative electrode rivaling on a polymer sheet.

[0031] Subsequently, after being immersed in the $LiBF_4$ 1.5 mol/l. solution (electrolytic solution) of (ethylene carbonate EC) / (propylene carbonate PC) / gamma-butyl lactone (gamma-BL) mixed solvent (EC/PC/gamma-BL =1/1/2) for 10 seconds and pulling up this layered product, sinking-in processing was performed at the

temperature of 100 degrees C for 2 hours. This layered product has the structure which the aluminum which is a positive electrode charge collector exposed to the top face, and the metal copper which is a negative electrode charge collector exposed to the inferior surface of tongue, packed back [which made the stainless steel sheet (10mm width of face, die length of 60mm) stick to these fields by pressure as an external connection terminal / whole] with polyethylene / aluminum / polyethylene terephthalate laminating sheet (lamination shaping; 120 degrees C of maximum temperatures, heating during 10 seconds), and produced the cell.

[0032] This cell was connected to the terminal of a charge and discharge test machine like the example 1, and charge and discharge were performed. As charge-and-discharge conditions, 75mA of currents performed charge by back 4.2V constant potential charge of 75mA of currents, and constant current, and discharge was performed by 2.7 V cuts. Charge-and-discharge effectiveness (quantity of electricity) was the time [2nd] 81% of first time and 99%, and the first-time amount of discharge was 195 mAh/g per carbon weight of a negative-electrode electrode. As a result of repeating a charge-and-discharge cycle furthermore, the percentage to the amount of first time charge-and-discharge discharge of the amount of discharge in 100 cycle (quantity of electricity) was 83%.

[0033]

[The example 1 of a comparison] The needle coke electrode (negative electrode) and $LiCoO_2$ which were produced in the example 1 The sheet which cut the electrode sheet (positive electrode) to 50mmx50mm, respectively was produced. The charge collector of this electrode sheet is a continuum, and is in the condition of having not performed perforated processing. Subsequently, it was the Pori (hexafluoropropylene-vinylidene fluoride) copolymer (1.4 % of the weight of hexafluoropropylene contents) melting push produced in the example 2, and after cutting a shaping sheet (45 micrometers of thickness, amount of electron beam irradiation 30Mrad) on 5.5cm square, the layered product consisted of structures where the paint film side of the electrode sheet of the positive electrode produced in the top and a negative electrode was made to rival on a polymer sheet. Subsequently, after being immersed in the $LiBF_4$ 1.5 mol/l. solution (electrolytic solution) of (ethylene carbonate EC) / (propylene carbonate PC) / gamma-butyl lactone (gamma-BL) mixed solvent (EC/PC/gamma-BL =1/1/2) for 10 seconds and pulling up the same actuation as an example 2, i.e., this layered product, sinking-in processing was performed at the temperature of 100 degrees C for 2 hours. This layered product has the structure which the aluminum which is a positive electrode charge collector exposed to the top face, and the metal copper which is a negative electrode charge collector exposed to the inferior surface of tongue, packed back [which made the stainless steel sheet (10mm width of face, die length of 60mm) stick to these fields by pressure as an external connection terminal / whole] with polyethylene / aluminum / polyethylene terephthalate laminating sheet (lamination shaping; 120 degrees C of maximum temperatures, heating during 10 seconds), and produced the cell. This cell was connected to the terminal of a charge and discharge test machine like the example 1, and charge and discharge were performed. As charge-and-discharge conditions, 75mA of currents performed charge by back 4.2V constant potential charge of 75mA of currents, and constant current, and discharge was performed by 2.7 V cuts. Charge-and-discharge effectiveness (quantity of electricity) was the time [2nd] 56% of first time and 91%, and the first-time amount of discharge was 68 mAh/g per carbon weight of a negative-electrode electrode. As a result of repeating a charge-and-discharge cycle furthermore, the percentage to the amount of first time charge-and-discharge discharge of the amount of discharge in 10 cycle (quantity of electricity) was 26%.

[0034]

[Effect of the Invention] This invention offers the solid polymer electrolyte cell excellent in the dependability of cell properties, such as charge-and-discharge effectiveness of a cell, the amount of discharge, and charge-and-discharge cycle nature, and stability.

[Translation done.]

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(54)【発明の名称】　電池およびその製造方法

(57)【要約】
【課題】　架橋構造を有する高分子固体電解質を用いた電池において充放電特性、性能安定性、安全性に優れた高性能電池及びその製造方法を提供する。
【解決手段】　架橋構造を有するポリフッ化ビニリデンおよび／またはフッ化ビニリデン系共重合体を含有する高分子固体電解質を介して正極と負極とが接合された電池において、少なくとも正極は集電体を有し、かつ少なくとも一方の集電体が有孔集電体である電池、並びに正極、及び負極をセパレターを挟んで積層し、積層体を形成した後に該積層体に電解液を含浸させる上記電池の製造方法。

【特許請求の範囲】

【請求項１】　架橋構造を有するポリフッ化ビニリデンおよび／またはフッ化ビニリデン系共重合体を含有する高分子固体電解質を介して正極と負極とが接合され、少なくとも正極は集電体を有し、且つ少なくとも一方の集電体が有孔集電体であることを特徴とする電池。

【請求項２】　少なくとも正極は集電体を有し、且つ少なくとも一方の集電体が有孔集電体である正極および負極を架橋構造を有するポリフッ化ビニリデンまたはフッ化ビニリデン系共重合体を含有するセパレータを挟んで積層して積層体を形成後、該積層体に電解液を含浸させることを特徴とする請求項１記載の電池の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は高分子固体電解質を用いた電池に関するものである。

【０００２】

【従来の技術】高分子固体電解質をイオン移動媒体とする電池は、従来の電解液をイオン移動媒体とする電池に比べ、液漏れがないため電池の信頼性、安全性が向上するとともに薄膜化や積層体形成の容易さ、電池形態の自由度が高いこと、パッケージの簡略化、軽量化が期待されている。

【０００３】この高分子固体電解質材料として、ポリエチレンオキシド、ポリプロピレンオキシドなどのポリアルキレンオキシドを中心とする材料、ポリアクリロニトリル、ポリフッ化ビニリデン系材料などイオン伝導性ポリマーに電解質、可塑剤を添加した材料が提案されている。この高分子固体電解質材料を用いて電池に利用する場合、高分子固体電解質が高イオン伝導性、高強度、耐熱性、電気化学的安定性などに優れることが好ましい。高分子固体電解質はマトリックスポリマー、電解質から構成された混合物またはこの材料に可塑剤を添加した混合物が用いられる。このマトリックスポリマーとして種々のポリマーが提案されている（例えば、Ｇｒａｙ著、ＳｏｌｉｄＰｏｌｙｍｅｒ　Ｅｌｅｃｔｒｏｌｙｔｅｓ（ＶＣＨパブリッシャー：１９９１年）記載のポリマー材料）。このうち特にマトリックスポリマーとしてポリフッ化ビニリデン、フッ化ビニリデン系共重合体などのフッ化ビニリデン系ポリマーを用いた高分子固体電解質材料が上記のいずれの点においても優れるため好ましい。

【０００４】高分子固体電解質を用いた電池は、シート状の電極と高分子固体電解質が積層された積層体や電極表面に高分子固体電解質層を塗布形成後積層させた積層体を所定の形状に加工して作製することができる。また、電極／高分子固体電解質／電極の各層を塗工によって形成する方法も提案されている。このように、シート積層や塗工などの方法が採用できることから製造プロセスが量産性に優れることが予想されている。また、従来の電解液系電池で起こりうる液漏れが実質的に起こらないため製造工程管理が容易であり、電極／高分子固体電解質／電極積層体の直列接続積層による高電圧化も期待されている。

【０００５】高分子固体電解質にポリ（ヘキサフルオロプロピレン－フッ化ビニリデン）共重合体を利用した電池が提案されている（米国特許第５２９６３１８号明細書）。この高分子固体電解質として前記フッ化ビニリデン系共重合体を用いているが、架橋構造を有さないため熱安定性に乏しく、溶融性、溶解性を有するため実用上の電池安全性で問題であった。また、この電池の作製方法として前記共重合体シートをセパレータとして用い非水溶媒系電解液に含浸して用いる場合、高温含浸において溶融や溶解が起こるため含浸温度が制限され、これによってポリマー中への電解液膨潤量が低く留まり、イオン伝導度が低かった。これを改善するため、架橋性モノマーをフッ化ビニリデン系ポリマー構造中に含有させモノマー重合による架橋構造形成が提案されている（米国特許第５４２９８９１号明細書）。ところが、残存モノマーや架橋性モノマーの重合体による電気化学副反応や、モノマーによっては微量の水による加水分解が生起し、それに伴って電気化学的副反応を起こすことがあった。また、このような架橋性モノマーをポリマーマトリックス中に分散させるために有機溶剤溶液を用いる必要があり、モノマーの重合を考慮して加工温度が制約されるという問題があり、この重合工程が煩雑であるため工業上問題であった。

【０００６】一方、有孔を有する集電体上に形成された電極を二次電池に用いることが提案され、集電体と電極活物質の付着性、集電性が改善されている（特公平７－７０３２７号公報）。また、フッ化ビニリデン系共重合体をポリマーマトリックスとした高分子固体電解質電池においてこの有孔集電体を用いることが提案されている（米国特許第５４７０３５７号明細書）。ところが前記のフッ化ビニリデン系共重合体を用いた高分子固体電解質と同様の残存モノマーや架橋性モノマー重合体による電気化学副反応が起こるなどの問題が残されていた。

【０００７】

【発明が解決しようとする課題】高分子固体電解質を用い充放電特性、性能安定性、安全性に優れた電池を提供することを目的とする。

【０００８】

【課題を解決するための手段】本発明者らは、高分子固体電解質を用いた固体電池の研究を進め、本発明の電池を完成した。すなわち、本発明は以下のとおりである。

（１）　架橋構造を有するポリフッ化ビニリデンおよび／またはフッ化ビニリデン系共重合体を含有する高分子固体電解質を介して正極と負極とが接合され、少なくとも正極は集電体を有し、且つ少なくとも一方の電極の集電体が有孔集電体であることを特徴とする電池。

（２）　少なくとも正極は集電体を有し、且つ少なくとも一方の集電体が有孔集電体である正極および負極を架橋構造を有するポリフッ化ビニリデンまたはフッ化ビニリデン系共重合体を含有するセパレータを挟んで積層して積層体を形成後、該積層体に電解液を含浸させることを特徴とする上記１の電池の製造方法。

【０００９】以下、本発明について詳細に説明する。本発明の電池は、集電体上に形成された正極と高分子固体電解質と負極から構成され、該負極は集電体を有していてもいなくとも良く、且つこの正極および負極の少なくとも一方の集電体が貫通孔を有する有孔集電体であることを特徴とする。この有孔集電体の貫通孔によって、正極／セパレータまたは高分子固体電解質／負極から構成される積層体の電極部および／またはセパレータ部への電解液含浸を容易にするだけでなく、電極の抵抗低減を図ることができる。本発明で述べるセパレータは、電解液を含浸し、膨潤することで高分子固体電解質として用いることのできる高分子固体電解質前駆体、すなわち電解液で含浸・膨潤される前の高分子固体電解質用樹脂からなる成形体である。

【００１０】本発明の電池において、少なくとも正極は、電極活物質粉末がバインダーで分散された混合体で形成された層に良電気伝導体からなる集電体が接合された構造を有することが好ましい。この電極活物質粉末がバインダーで分散された混合体で形成された層は集電体の片面だけに存在していても良いし、両面に存在していても良い。

【００１１】この有孔集電体を有する電極の代表的な作製方法としては、メッシュ、織布、不織布、焼結体などの孔を含有する構造の集電体に電極活物質層を接合する方法、連続体からなる集電体に予め孔を形成させて電極活物質層を接合する方法、連続体からなる集電体に電極活物質層を接合した後集電体の孔開け加工を行う方法などが挙げられる。この集電体材料として、正極には酸化安定性に優れた材料が好ましく、アルミニウム、ステンレススチール、ニッケル、炭素などが用いられ、特にアルミニウムが好ましい。また負極の集電体材料として、金属銅、ステンレススチール、ニッケル、炭素などが用いられ、特に金属銅が好ましい。

【００１２】本発明で用いられる有孔集電体として、平均孔径１．５mm以下、１００Å以上の貫通した孔を有し、開口率５％以上、９０％以下であることが好ましい。平均孔径が１．５mmより大きいと集電体の集電作用が充分でなく、電極の機械的強度を低下させることから好ましくない。また平均孔径が１００Å未満では電解液含浸が困難となるため好ましくない。開口率５％未満の場合、集電体と電極活物質層との密着性向上の効果や、電極の抵抗低減作用が充分でなく、また電解液含浸が困難となり、開口率９０％を越えると集電体の集電作用が充分でなくなることから好ましくない。さらに集電体の厚さは５００μm以下であることが好ましい。５００μmより厚いと集電体自体の見かけ容積が大きくなり、これを用いて構成した電池の体積エネルギー密度が低下するため小型軽量二次電池には好ましくない。

【００１３】また、本発明における高分子固体電解質のポリマーマトリックスは架橋構造を有するポリフッ化ビニリデンおよび／またはフッ化ビニリデン系共重合体を含有することが必要である。フッ化ビニリデン系共重合体としては、例えば、ポリ（ヘキサフルオロプロピレン－ビニリデンフロライド）共重合体、ポリ（パーフルオロビニルエーテル－ビニリデンフロライド）共重合体、ポリ（テトラフルオロエチレン－ビニリデンフロライド）共重合体、ポリ（ヘキサフルオロプロピレンオキシド－ビニリデンフロライド）共重合体、ポリ（ヘキサフルオロプロピレンオキシド－テトラフルオロエチレン－ビニリデンフロライド）共重合体、ポリ（ヘキサフルオロプロピレン－テトラフルオロエチレン－ビニリデンフロライド）共重合体、ポリ（フルオロエチレン－ビニリデンフロライド）共重合体が挙げられる。これらポリフッ化ビニリデンおよびフッ化ビニリデン系共重合体は単独体でも混合体でも用いることができる。本発明で用いられる高分子固体電解質のポリマーマトリックスにおけるフッ化ビニリデンユニットの含有量は２０重量％以上であることが好ましく、５０重量％以上であることがより好ましい。また、本発明の電池における高分子固体電解質ポリマーマトリックスとして、ポリフッ化ビニリデンおよび／またはフッ化ビニリデン系共重合体と他のポリマーとを積層した積層体も使用可能である。

【００１４】本発明においては高分子固体電解質が架橋構造を有することにより耐熱性、寸法安定性に優れるとともに高い電解液含量の材料が得られ、これが高イオン伝導度をもたらし好ましい材料となる。高分子固体電解質のポリマーマトリックスが架橋していないポリマーで形成されている場合には、電池の急速充電や急速放電の場合や外部加熱において溶融、流動しやすく、これに伴って電極間短絡を起こすことがあり電池の安全上問題があった。一方本発明の架橋構造を有するフッ化ビニリデン系ポリマーを含有する高分子固体電解質ではこのような問題を回避することができる。

【００１５】ポリフッ化ビニリデン系樹脂は通常リニア構造を有し、この樹脂を架橋化することにより本発明のポリフッ化ビニリデン系樹脂のマトリックスポリマーを作製する。この架橋方法として例えば、電子線、ガンマ線、Ｘ線、紫外線、赤外線などの輻射エネルギー照射、ラジカル開始剤を含有させて反応架橋させる方法、アルカリ処理（脱ＨＦ）後反応性基を反応架橋させる方法、などを用いることができる。電子線照射を用いる場合の架橋条件として、この照射量が充分でない場合架橋効果が充分でなく、照射量が多すぎる場合ポリマー構造が崩壊するため好ましくない。この照射量は５Ｍｒａｄ以上

１００Ｍｒａｄ以下であることが好ましく、さらに好ましくは5Ｍｒａｄ以上８０Ｍｒａｄ以下である。

【００１６】この架橋構造形成はリニアポリマー可溶性有機溶剤への溶解性により確認することができる。つまり、架橋構造が形成されたポリフッ化ビニリデン系樹脂は可溶性有機溶剤に溶解しない成分を有し、均一溶解しないことから架橋構造の有無を判別することができる。本発明において架橋構造を有するとは、可溶性有機溶剤に溶解しない成分を有し、均一溶解しないものをいう。この可溶性溶剤はポリマー種類により異なるため限定されないが、例えばＮ－メチルピロリドン、クロロホルム、ジクロロメタン、ジクロロエタン、アセトン、テトラヒドロフラン、ジメチルホルムアミド、ジメチルスルホキシド、ジメチルアセトアミドなどの溶剤で判別することができる。

【００１７】高分子固体電解質として、バルク形状、貫通孔を有する多孔体、独立泡を有する発泡体などに電解液を含浸して形成した高分子固体電解質を用いることができる。このうち独立泡を含有する発泡体に電解液を含浸した高分子固体電解質や貫通孔を有する多孔質ポリマーに電解液を含浸させた高分子固体電解質は構造中に液相ドメインを有し電解液で含浸・膨潤されたポリマー相との複合構造を形成する。この液相の存在により高分子固体電解質のイオン伝導度が高められ、全体として高いイオン伝導度をもたらすことから好ましい。

【００１８】本発明で用いる電解液に含有される電解質として、有機酸、有機塩、無機酸、無機塩のいずれも使用可能である。この例としてテトラフルオロホウ酸、過塩素酸、硫酸、リン酸、フッ化水素酸、塩酸などの無機酸、トリフルオロメタンスルホン酸、トリフツオロプロピルスルホン酸、ビス（トリフルオロメタンスルホニル）イミド酸、酢酸、チルフルオロ酢酸、プロピオン酸などの有機酸、およびこれら有機酸、無機酸の金属塩が挙げられる。これらは単独で用いることもできるし、複数の電解質を混合して用いることもできる。さらにパーフルオロスルホン酸系ポリマーやパーフルオロカルボン酸系ポリマーあるいはこれらの金属塩も本発明の電解質として使用できる。これら電解質のカチオンとしてプロトン、アルカリ金属カチオン、アルカリ土類金属カチオン、遷移金属カチオン、希土類金属カチオンなどから選ばれるカチオンを一種類で、また複数混合して使用することができる。このカチオン種は使用する用途によって異なるため限定されない。例えば、本発明の高分子固体電解質をリチウム電池に使用する場合は、添加する電解質としてリチウム塩を使用することが好ましい。特にリチウム二次電池に利用する場合、充放電を繰り返し行う必要から、電解質に電気化学的安定性に富むリチウム塩を選ぶことが好ましく、この例として、CF_3SO_3Li、$C_4F_9SO_3Li$、$(CF_3SO_2)_2NLi$、$LiBF_4$、$LiPF_6$、$LiClO_4$、$LiAsF_6$、$Li(C_6H_5)_4B$、$Li_2B_{10}Cl_{10}$、$Li_2B_{12}Cl_{12}$等を挙げることができる。

【００１９】また、本発明の高分子固体電解質に含浸した電解質のイオン解離促進、電解質の含浸性を高める、高分子固体電解質の加工性向上などの目的で可塑剤を含有させることができる。本発明の架橋された高分子固体電解質では高い可塑剤含有量においても力学的強度を損なわない特徴を有する。この可塑剤含量は可塑剤の種類、フッ化ビニリデン系ポリマーの種類、構造によって異なるため限定されないが、通常は高分子固体電解質重量の９８％以下である。さらに好ましくは９７％以下である。

【００２０】この可塑剤の例として、エチレンカーボネート、プロピレンカーボネート、ビチレンカーボネートなどの環状カーボネート、ジメチルカーボネート、メチルエチルカーボネート、メチルエチルカーボネートなどの鎖状カーボネート、テトラヒドロフラン、メチルテトラヒドロフランなどのエーテル、γ－ブチルラクトン、プロピオラクトン、酢酸メチルなどのエステル、アセトニトリル、プロピオニトリルなどのニトリル化合物、炭化水素などの有機低分子化合物、シリコンオイル、オリゴエチレングリコール、ポリエチレンオキシド、ポリプロピレンオキシドなどの脂肪族エータル化合物、ポリアクリロニトリル、脂肪族ポリエステル、脂肪族ポリカーボネートなどの極性基含有高分子有機化合物を挙げることができる。

【００２１】以上説明した電解質、可塑剤からなる電解液を架橋体と未架橋体の混合したフッ化ビニリデン系樹脂からなる成形体に含浸することによって本発明の高分子固体電解質を作製する。次に本発明の高分子固体電解質を介して接合する電極について説明する。たとえば電池がリチウム電池の場合、電極の正極および負極にリチウムイオン吸蔵放出可能な物質を用いる。この正極物質として、負極に対して高い電位を有する材料、この例としては、$Li_{1-x}CoO_2$、$Ln_{1-x}NiO_2$、$Li_{1-x}Mn_2O_4$、$Li_{1-x}MO_2$ $(0<x<1)$、Ｍは Ｃｏ、Ｎｉ、Ｍｎ、Ｆｅの混合体を表す。）、$Li_{2-y}Mn_2O_4$ $(0<y<2)$、結晶性$Li_{1-x}V_2O_5$、アモルファス状$Li_{2-y}V_2O_5$ $(0<y<2)$、$Li_{1.2-x}Nb_2O_5$ $(0<x'<1.2)$などの酸化物、$Li_{1-x}TiS_2$、$Li_{1-x}MoS_2$、$Li_{3-z}NbSe_3$ $(0<z<3)$などの金属カルコゲナイド、ポリピロール、ポリチオフェン、ポリアニリン、ポリアセン誘導体、ポリアセチレン、ポリチエニレンビニレン、ポリアリレンビニレン、ジチオール誘導体、ジスルフィド誘導体などの有機化合物を挙げることができる。

【００２２】また負極として、上記正極に対して低い電位を有する材料を用いる。この例として、金属リチウム、アルミ・リチウム合金、マグネシウム・アルミ・リチウム合金などの金属リチウム、ＡｌＳｂ、Mg_2G

e、$NiSi_2$などの金属間化合物、グラファイト、コークス、低温焼成高分子などの炭素系材料、SnM系酸化物（MはSi，Ge，Pbを表す。）、$Si_{1-y}M'_yO_z$（M′はW，Sn，Pb，Bなどを表す。）の複合酸化物、酸化チタン、酸化鉄などの金属酸化物のリチウム固溶体、Li_7MnN_4、Li_3FeN_2、$Li_{3-x}Co_xN$、$Li_{3-x}NiN$、$Li_{3-x}Cu_xN$、Li_3BN_2、Li_3AlN_2、Li_3SiN_3の窒化物などのセラミックス等が挙げられる。ただし、リチウムイオンを負極で還元して金属リチウムとして利用する場合は、導電性を有する材料であればよいので、上記に限定されない。

【0023】本発明の電池に用いる正極および負極は上記の材料を所定の形状に成形加工して用いられる。この形態として連続体または粉末材料のバインダー分散体のいずれも使用可能である。前者の連続体の成形方法として、電解析出、電解溶解、蒸着、スパッタリング、CVD、溶融加工、焼結、圧縮などが用いられる。また、後者の場合は粉末状の電極物質をバインダーとともに混合して成形する。このバインダー材料として、ポリビニリデンフロライド、ポリ（ヘキサフルオロプロピレン－ビニリデンフロライド）共重合体などポリフッ化ビニリデン系樹脂、ポリテトラフルオロエチレン、などのフッ素系ポリマー、スチレン－ブタジエン共重合体、スチレン－アクリロニトリル共重合体、スチレン－アクリロニトリル－ブタジエン共重合体などの炭化水素系ポリマー、ポリマー前駆体、金属などが用いられ、本発明の架橋構造を有するポリフッ化ビニリデン系樹脂をバインダーに用いることもできる。

【0024】本発明の電池の作製方法として、①予め電解液をポリマーマトリックスに含浸して作製した高分子固体電解質と正極および負極を積層して積層体を形成してユニットセルを構成する方法、②高分子固体電解質の前駆体であるセパレータと正極および負極を積層して積層体を形成した後、電解液をセパレータに含浸・膨潤させてセパレータを高分子固体電解質に変換させてユニットセルを形成する方法、があり、いずれも可能である。特に後者の場合、電解液が雰囲気中に存在する湿度で劣化しやすいことを考慮すれば雰囲気管理工程が簡略でき工業上好ましい。また、電解液含浸により、電極空孔部分に電解液が充填され、これによって電極抵抗低減や電極と高分子固体電解質の電気化学的接合が良好となる効果も考えられることから、前者のユニットセル作製方法においても、積層体形成後、電解液含浸を施すことは有効である。このような本発明のユニットセルの作製工程における電解液含浸は、有孔集電体を有する電極が電極活物質粉末とバインダーからなる構造である場合に好ましく行われることから、有孔集電体を有する電極は電極活物質粉末とバインダーからなる構造であることが好ましい。有孔集電体を有する電極が連続体の場合はセパレータへの含浸が難しくなる。しかしながら、ユニットセル作製工程において電極積層後、電解液を含浸させない場合においても、集電体と電極層との接続する電気抵抗は低減できる効果を有することから、電極材料として種々の材料を用い、様々な方法で本発明の電池が構成できる。

【0025】本発明の電池は、特にリチウムイオン電池に好適であるが、これにとどまらず鉛電池、アルカリ電池、ニッケル水素電池など種々の電池に応用できるため産業上有用である。

【0026】

【発明の実施の形態】以下、実施例で本発明を詳細に説明する。

【0027】

【実施例1】平均粒径10μmのニードルコークス粉末をカルボキシメチルセルロース溶液とスチレンブタジエンラテックス（旭化成工業（株）製、L1571　商品名）分散液混合体に分散してスラリーを作製し、金属銅シート（18μm厚）に塗布乾燥して膜厚120μmの塗膜（片面塗工）を形成した。該塗膜中の組成はニードルコークス（NC）／カルボキシメチルセルロース／スチレンブタジエン＝100／0．8／2とした。この電極シートの集電体面から針差しにより平均直径150μmの孔を1cm^{2}当たり625個開けた有孔集電体からなる電極を作製した。一方、平均粒径10μmの$LiCoO_2$粉末とカーボンブラックをポリフッ化ビニリデンのN－メチルピロリドン溶液（5重量%）に混合分散してスラリーを作製した。このスラリーをアルミ箔（20μm厚）に塗布（片面塗工）乾燥して膜厚100μmの塗膜を作製した。なおスラリーの固形分重量組成は、$LiCoO_2$（85%）、カーボンブラック（8%）、ポリマー（7%）とした。次いで、電極シートのアルミニウム集電体側から、1cm^{2}当たり625個（平均直径150μm）の孔を針刺しにより形成して有孔集電体からなる電極を作成した。次いで、該NC電極および$LiCoO_2$電極をそれぞれ5cm角に切断した。

【0028】ポリ（ヘキサフルオロプロピレン－フッ化ビニリデン）共重合体（ヘキサフルオロプロピレン含量5重量%）を溶融押しだし成形して膜厚110μmのシートを作製した。該ポリマーシートに電子線照射（照射量10Mrad）を施した後フロン（HFC134a）を含浸させ（含浸重量7%）含浸状態で加熱して発泡体を作製した（発泡後膜厚220μm）。該シートをエチレンカーボネート（EC）／プロピレンカーボネート（PC）／γ－ブチルラクトン（γ－BL）混合溶媒（EC／PC／γ－BL＝1／1／2）の$LiBF_4$ 1．5mol／リットル溶液に1時間浸漬して電解液を含浸させて高分子固体電解質シートを作製した。

【0029】該高分子固体電解質シートを5．5cm角に切断した後、前記の5cm角に切断したNC電極、L

ｉＣｏO_2 電極の塗膜面を高分子固体電解質に向かい合わせる構造で張り合わせて電池積層体を作製した。ついで該積層体にエチレンカーボネート（ＥＣ）／プロピレンカーボネート（ＰＣ）／γ－ブチルラクトン（γ－ＢＬ）混合溶媒（ＥＣ／ＰＣ／γ－ＢＬ＝１／１／２）のＬｉＢF_4 １．５ｍｏｌ／リットル溶液に１０秒間浸漬させた。電解液含浸後の積層体から電極取り出し用電極としてステンレスシートを金属銅シート面およびアルミニウムシート面に接合し、さらにポリエチレン／アルミニウム／ポリエチレンテレフタレート積層シートでパッケージしてシート電池を作製した。該電池を充放電試験機（北斗電工１０１ＳＭ６型）の端子に接続して充放電を行った。充放電条件として、充電は電流２５ｍＡ、定電流の後４．２Ｖ定電位充電、放電は電流２５ｍＡで２．７Ｖカットで行った。充放電効率（電気量）は初回８０％、２回目９８％であり、初回の放電量は負極電極の炭素重量当たり２１６ｍＡｈ／ｇであった。さらに充放電サイクルを繰り返した結果、１００サイクルにおける放電量（電気量）の初回充放電放電量に対する割合は８４％であった。

【００３０】

【実施例２】実施例１で使用した金属銅およびアルミニウム集電体シートそれぞれに、予め直径１５０μｍの孔を１ｃm^2 当たり６２５個形成した有孔集電体シートを作製し、この片面に実施例１と同様に塗布形成してニードルコークス電極（負極）とＬｉＣｏO_2 電極（正極）を作製した。有孔集電体上に電極塗膜を形成した正極および負極の電極シートを、それぞれ５ｃｍ角に切断した。ポリ（ヘキサフルオロプロピレン－フッ化ビニリデン）共重合体（ヘキサフルオロプロピレン含量１．４重量％）を溶融押しだし成形して膜厚４５μｍのシートを作製した。該ポリマーシートに電子線照射（照射量３０Ｍｒａｄ）を施した。電子線照射後のシートを５．５ｃｍ角に切断した後、上で作製した正極および負極の電極シートの塗膜面をポリマーシートに張り合わせる構造で積層体を構成した。

【００３１】次いで、該積層体をエチレンカーボネート（ＥＣ）／プロピレンカーボネート（ＰＣ）／γ－ブチルラクトン（γ－ＢＬ）混合溶媒（ＥＣ／ＰＣ／γ－ＢＬ＝１／１／２）のＬｉＢF_4 １．５ｍｏｌ／リットル溶液（電解液）に１０秒間浸漬して引き上げた後１００℃の温度で２時間含浸処理を施した。該積層体は、上面に正極集電体であるアルミニウムが露出し、下面に負極集電体である金属銅が露出した構造を有し、これらの面に外部接続端子としてステンレスシート（１０ｍｍ幅、長さ６０ｍｍ）を圧着させた後全体をポリエチレン／アルミニウム／ポリエチレンテレフタレート積層シートでパッケージ（ラミネート成形；最高温度１２０℃、１０秒間加熱）して電池を作製した。

【００３２】該電池を実施例１と同様に充放電試験機の端子に接続して充放電を行った。充放電条件として、充電は電流７５ｍＡ、定電流の後４．２Ｖ定電位充電、放電は電流７５ｍＡで２．７Ｖカットで行った。充放電効率（電気量）は初回８１％、２回目９９％であり、初回の放電量は負極電極の炭素重量当たり１９５ｍＡｈ／ｇであった。さらに充放電サイクルを繰り返した結果、１００サイクルにおける放電量（電気量）の初回充放電放電量に対する割合は８３％であった。

【００３３】

【比較例１】実施例１で作製したニードルコークス電極（負極）およびＬｉＣｏO_2 電極シート（正極）をそれぞれ５０ｍｍ×５０ｍｍに切断したシートを作製した。この電極シートの集電体は連続体であり、有孔加工を施していない状態である。次いで、実施例２で作製したポリ（ヘキサフルオロプロピレン－フッ化ビニリデン）共重合体（ヘキサフルオロプロピレン含量１．４重量％）溶融押しだし成形シート（膜厚４５μｍ、電子線照射量３０Ｍｒａｄ）を５．５ｃｍ角に切断した後、上で作製した正極および負極の電極シートの塗膜面をポリマーシートに張り合わせた構造で積層体を構成した。次いで、実施例２と同様の操作、すなわち該積層体をエチレンカーボネート（ＥＣ）／プロピレンカーボネート（ＰＣ）／γ－ブチルラクトン（γ－ＢＬ）混合溶媒（ＥＣ／ＰＣ／γ－ＢＬ＝１／１／２）のＬｉＢF_4 １．５ｍｏｌ／リットル溶液（電解液）に１０秒間浸漬して引き上げた後１００℃の温度で２時間含浸処理を施した。該積層体は、上面に正極集電体であるアルミニウムが露出し、下面に負極集電体である金属銅が露出した構造を有し、これらの面に外部接続端子としてステンレスシート（１０ｍｍ幅、長さ６０ｍｍ）を圧着させた後全体をポリエチレン／アルミニウム／ポリエチレンテレフタレート積層シートでパッケージ（ラミネート成形；最高温度１２０℃、１０秒間加熱）して電池を作製した。該電池を実施例１と同様に充放電試験機の端子に接続して充放電を行った。充放電条件として、充電は電流７５ｍＡ、定電流の後４．２Ｖ定電位充電、放電は電流７５ｍＡで２．７Ｖカットで行った。充放電効率（電気量）は初回５６％、２回目９１％であり、初回の放電量は負極電極の炭素重量当たり６８ｍＡｈ／ｇであった。さらに充放電サイクルを繰り返した結果、１０サイクルにおける放電量（電気量）の初回充放電放電量に対する割合は２６％であった。

【００３４】

【発明の効果】本発明は、電池の充放電効率、放電量、充放電サイクル性などの電池特性の信頼性、安定性に優れた高分子固体電解質電池を提供する。